Title	Precipitation behavior of highly Sr-doped LaPO4 in phosphoric acid solutions
Author(s)	Hatada, Naoyuki; Nose, Yoshitaro; Kuramitsu, Akiko; Uda, Tetsuya
Citation	Journal of Materials Chemistry (2011), 21(24): 8781-8786
Issue Date	2011
URL	http://hdl.handle.net/2433/156799
Right	© Royal Society of Chemistry 2011.
Type	Journal Article
Textversion	author

Precipitation behavior of highly Sr-doped $LaPO_4$ in phosphoric acid solutions

Naoyuki Hatada,*[a] Yoshitaro Nose,[a] Akiko Kuramitsu[a] and Tetsuya Uda*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

The precipitation condition of $LaPO_4$ in phosphoric acid solution was investigated under both atmospheric and humidified conditions. The crystal morphology, Sr doping level, H_2O incorporation, and high temperature stability of Sr-doped $LaPO_4$ precipitates were also analyzed. Increasing pH_2O from 0.01 to 1 atm extends the precipitation region of $LaPO_4$ in phosphoric acid solutions toward higher temperatures by nearly 100 °C. Under such conditions (*e.g.* T = 250 °C and pH_2O = 1 atm), it is possible to obtain aggregated crystals up to 200 μm. The Sr doping level in $LaPO_4$ shows a strong dependence on the precipitation ratio of La, X_{La}. The Sr doping level is higher in the low X_{La} region, reaching 20 mol% at maximum. This value is one order of magnitude higher than the previously reported solubilities. It was confirmed H_2O is certainly incorporated in the bulk by Sr doping. The solubility of Sr in $LaPO_4$ would be sufficiently high (at least 20.1 %) even at 600 °C; however, it becomes considerably lower at 1200 °C.

1. Introduction

In recent years, lanthanum orthophosphate ($LaPO_4$) has received attention because of its potential application as a solid electrolyte in fuel cells.[1–4] It exhibits protonic conductivity on the order of 10^{-4} S cm^{-1} at 700 °C when La is partially substituted with alkaline earth metals such as Sr. [1,5] For practical use, however, further enhancement of the conductivity is necessary.

Amezawa *et al*. reported that the conductivity of Sr-doped $LaPO_4$ increased with increasing the dopant concentration.[6] They also reported that the solubility of Sr in $LaPO_4$, represented by the molar ratio Sr/(La+Sr), was approximately 2 %.[7] With higher Sr mixing ratios, a secondary phase, $Sr_2P_2O_7$, appeared and the conductivity decreased with increasing Sr concentration. Thus, the low solubility of Sr is an obstacle to enhancing the conductivity of $LaPO_4$.

While the solubility research described above was conducted with samples prepared by solid state reaction and sintered at 1200 °C,[7] there are several reports of different Sr doping levels with different synthesis temperatures. Tyholdt *et al*. reported the solubility of Sr in $LaPO_4$ to be ~1 % with samples sintered at 1450 °C.[8] Gallini *et al*. prepared 5 % Sr-doped $LaPO_4$ by combustion synthesis followed by calcination at 800 °C.[3] Schatzmann *et al*. synthesized Sr-doped $LaPO_4$ by adding $La(NO_3)_3{\cdot}6H_2O$ and $Sr(NO_3)_2$ to heated phosphoric acid at 150 °C, followed by precipitation of $LaPO_4$ within 30 minutes.[9] With this method, at least 4 % Sr-doped $LaPO_4$ was obtained. These results suggest that the solubility of Sr would be higher at lower temperatures. Besides temperature, water vapor pressure may also affect the solubility of Sr. When Sr is doped into $LaPO_4$, a certain amount of water is also introduced into $LaPO_4$ as represented by the following expression:

$$(1-x)\,LaPO_4 + (x/2)\,Sr_2P_2O_7 + (y/2)\,H_2O \rightarrow La_{1-x}Sr_xH_yPO_{4-(x/2)+(y/2)}. \quad (1)$$

Therefore, Sr-doped $LaPO_4$ ($La_{1-x}Sr_xH_yPO_{4-(x/2)+(y/2)}$) would be stabilized with higher water vapor pressure. However, the relationship between the solubility of Sr and these parameters has not been clarified yet.

When the above synthesis methods are used, powder samples are generally obtained. For use as electrolytes, they need to be sintered at over 1000 °C for densification. This heat treatment is expected to limit the solubility of Sr to approximately 2 %. [7] Therefore, to synthesize highly Sr-doped $LaPO_4$, avoiding high temperature heat treatments in syntheses would also be important.

Synthesis of single crystals of rare earth ultraphosphates (REP_5O_{14}, RE: rare earth elements) in phosphoric acid solutions has been the subject of intensive investigations since the 1970s, for the purpose of using them as laser materials. [10,11] In the series of these researches, Chudinova *et al*. investigated the $La_2O_3 – P_2O_5 – H_2O$ system and reported that $LaPO_4$ precipitated in phosphoric acid solutions at below 160 °C. [12] Although there is no detailed information on the precipitation behavior of $LaPO_4$, it is possible to obtain Sr-doped $LaPO_4$ with sufficiently large size and density for use as electrolytes directly.

Therefore, synthesis of $LaPO_4$ in homogeneous phosphoric acid solutions was performed in this research. The conditions (temperature and water vapor pressure) where $LaPO_4$ can be precipitated in phosphoric acid solutions were investigated. The morphology of precipitates was also observed. Then, the condition dependence of the Sr doping level was analyzed to reveal the optimum condition for obtaining highly Sr-doped $LaPO_4$. The effectiveness of Sr doping was verified by observing unit cell volume changes by doping and the evaporation of H_2O which had been incorporated into $LaPO_4$

during the synthesis. Finally, the stability of Sr-doped $LaPO_4$ at high temperatures was investigated.

2. Experimental

2.1. Synthesis

Undoped and Sr-doped $LaPO_4$ were synthesized by precipitation in homogeneous phosphoric acid solutions containing La_2O_3 and $SrCO_3$. La_2O_3 (99.99%, Nacalai Tesque), $SrCO_3$ (99.99%, Wako Pure Chemical Industries), and H_3PO_4 (85%, Nacalai Tesque) were mixed in a perfluoroalkoxy (PFA) beaker and held at 190 °C in a furnace for several days to obtain a transparent solution. Then temperature and water vapor pressure were changed and held for a predetermined period of time to precipitate $LaPO_4$. The temperature was set between 120 °C and 250 °C, and the water vapor pressure was set to approximately 0.01 atm (atmospheric conditions) or 1 atm (humidified conditions). Synthesis parameters are summarized in Table 1 and Table 2.

For humidification, the apparatus shown in Fig. 1 was used. The whole apparatus was placed in a furnace kept at a constant temperature. A beaker was put on a stainless steel floor plate and covered with a stainless steel box with a capacity of 2.64 L. A 4-m-long spiral tube was attached to a side wall of the box. Liquid water was fed to the box through the spiral tube so that it evaporated before reaching the box. The liquid water feed rate was 0.1 mL/min, which was equivalent to 0.18 L-H_2O(g)/min at 120 °C and 0.24 L-H_2O(g)/min at 250 °C. The apparatus was not sealed tightly so that the inner gas was able to flow out through the narrow gap between the box and the floor plate when the inner pressure exceeded 1 atm. Therefore, the water vapor pressure inside the box was expected to be 1 atm.

After the predetermined precipitation period, the beaker was cooled down to room temperature. In general, there were precipitates on the bottom of the beaker and the transparent solution above them. The solution was collected for the chemical analysis. The precipitates were washed well with hot water (~90 °C).

2.2. Characterization

Phase identification was carried out *via* X-ray powder diffraction (XRD) analysis on PANalytical X'Pert-Pro MPD using Cu Kα radiation at room temperature. The unit cell volume of samples was evaluated by the Rietveld method using X'Pert HighScore Plus (Version 2.2c) software. The morphology of precipitates was investigated using KEYENCE VE-7800 scanning electron microscopy (SEM). Chemical analysis of solutions and precipitates was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on Seiko Instruments SPS4000.

The amount of H_2O evaporated from samples was determined by the Karl Fischer titration method. The samples were dried in advance at 600 °C for 50 h in the air (pH_2O ~ 0.01 atm) to eliminate residual water and phosphoric acid on the surface of samples. The protons responsible for the proton conduction were still expected to remain in the samples, judging from the reported pH_2O dependence of the conductivity at 600 °C. [6] Then each sample was held at 800 °C under dry nitrogen flow (200 mL/min) to be dehydrated. The nitrogen which contains the released H_2O was transferred to the Karl Fischer moisture titrator to determine the amount of H_2O evaporated from the sample. For this, Kyoto Electronics Manufacturing MKC-510N (Karl-Fischer moisture titrator) and ADP-512S (evaporator) were utilized.

Table 1 Initial compositions of solutions for the synthesis of $LaPO_4$.

Abbrev.	Starting materials	Initial composition	
		Molar ratio La : Sr : P	$\frac{Sr}{La+Sr}$ (mol%)
Sr0	La_2O_3, $SrCO_3$, H_3PO_4	1.00 : 0.00 : 15	0
Sr4		0.96 : 0.04 : 15	4
Sr8		0.92 : 0.08 : 15	8

Table 2 Dissolution and precipitation conditions for the synthesis of $LaPO_4$.

Abbrev.	Dissolution		Precipitation	
	Temp. (°C)	pH_2O (atm)	Temp. (°C)	pH_2O (atm)
A230	190	~0.01	230	~0.01
A140			140	~0.01
A120			120	~0.01
H250			230	~1
H140			140	~1
H120			120	~1

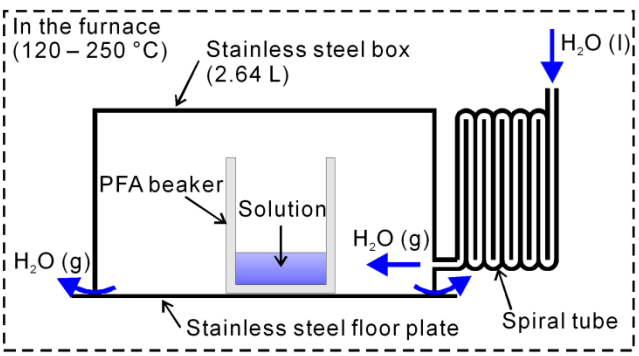

Fig. 1 Schematic illustration of the apparatus used for humidification during the precipitation of $LaPO_4$.

3. Results and discussion

3.1. Precipitation condition and crystal morphology of $LaPO_4$ and LaP_3O_9

The precipitation condition of $LaPO_4$ was investigated using solutions with the composition Sr0. Experiments were performed under both atmospheric (A230, A140) and humidified (H250, H140) conditions. Fig. 2 shows the X-ray diffraction patterns of the precipitates obtained under each condition. Under the atmospheric conditions, monazite-type $LaPO_4$ was obtained at 140 °C while LaP_3O_9 was obtained at 230 °C. This is consistent with the results reported by

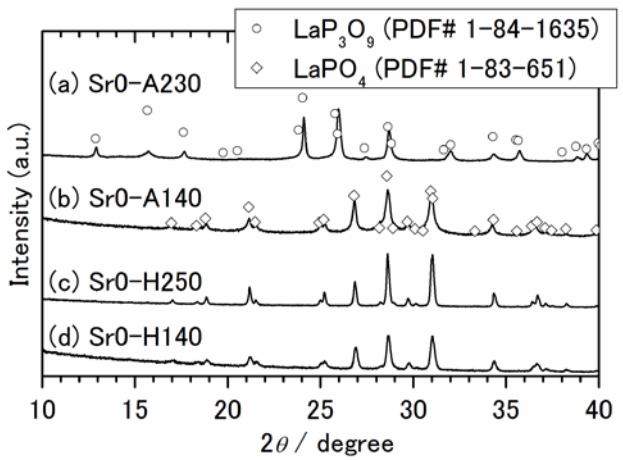

Fig. 2 X-ray powder diffraction patterns of undoped $LaPO_4$ and LaP_3O_9 precipitates obtained under the conditions (a) A230, (b) A140, (c) H250, and (d) H140.

Chudinova *et al.* [12] Under the humidified conditions, monazite-type $LaPO_4$ was obtained both at 250 °C and 140 °C. With these results, the precipitation region of $LaPO_4$ was drawn on the temperature – pH_2O plane (Fig. 3). As indicated in the figure, increasing pH_2O from 0.01 to 1 atm extends the precipitation region of $LaPO_4$ toward higher temperatures by nearly 100 °C. At 1 atm H_2O, $LaPO_4$ can be obtained even at 250 °C, where LaP_3O_9 will be obtained at lower pH_2O such as 0.2 atm. The analogous phenomenon for LaP_3O_9 and LaP_5O_{14} was reported in detail by Balagina *et al.* [13]

Fig. 4 shows SEM images of undoped $LaPO_4$ and LaP_3O_9 precipitates. Under the conditions A140 and H140, $LaPO_4$ precipitates were rice-shaped particles with a size range of 500 nm – 1 μm. In contrast, under H250 condition, the $LaPO_4$ precipitates were dense aggregates of well-shaped crystals up to 200 μm. Thus, the precipitation temperature had a marked effect on the crystal growth of $LaPO_4$. Higher precipitation temperatures, in combination with humidification, may enable direct syntheses of dense $LaPO_4$ electrolytes in phosphoric acid solutions.

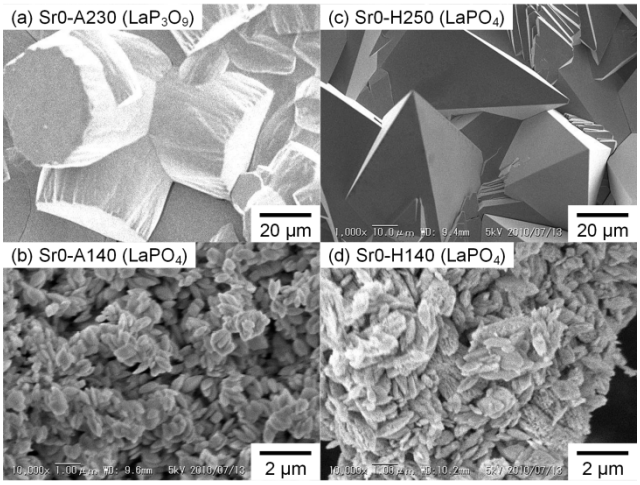

Fig. 4 SEM images of undoped $LaPO_4$ and LaP_3O_9 precipitates obtained under the conditions (a) A230, (b) A140, (c) H250, and (d) H140.

3.2. Optimum condition for obtaining highly Sr-doped $LaPO_4$

Attempts to synthesize Sr-doped $LaPO_4$ were carried out using solutions with the compositions Sr4 and Sr8. Experiments were performed in the precipitation region of $LaPO_4$ (see Fig. 3) under both atmospheric (A120) and humidified (H250, H120) conditions. The precipitation period was varied to observe changes in the composition of precipitates and solutions with time. In each condition, single phase $LaPO_4$ was precipitated, as confirmed by X-ray diffraction.

Fig. 5 shows the change in the composition of the solutions with time measured by ICP. The concentrations of La and Sr decreased with time. In particular, under H120 condition, the concentrations decreased rapidly by 2 – 3 orders. This indicates that the solubility of $LaPO_4$ in phosphoric acid solutions is especially low under H120 condition, or the driving force for the precipitation is strong under that condition. This result corresponds well to the fact that H120 condition is quite deep in the precipitation region of $LaPO_4$ in Fig. 3. Under A120 condition, the changes in the

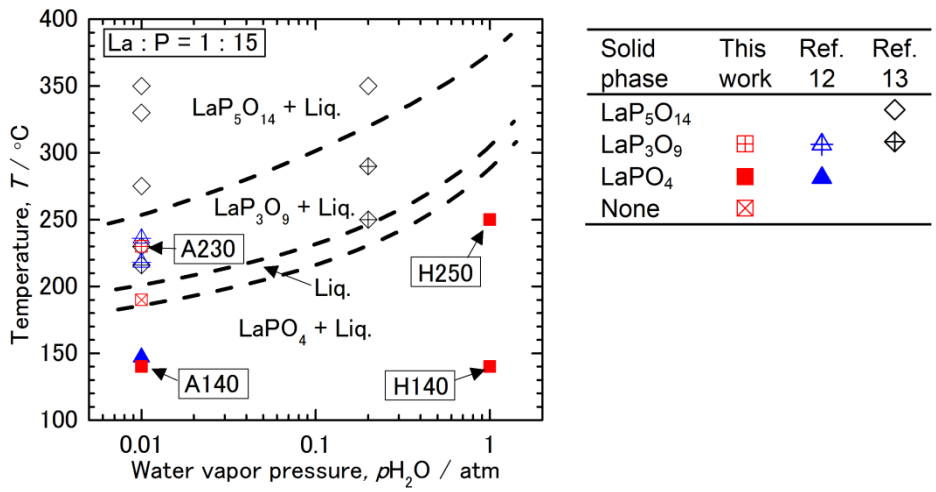

Fig. 3 Phase stability diagram of the La_2O_3 – P_2O_5 – H_2O system with a constant La/P ratio (La : P = 1 : 15). In addition to the results obtained in this study, previous results reported by Chudinova *et al.* [12] and Balagina *et al.* [13] are also shown.

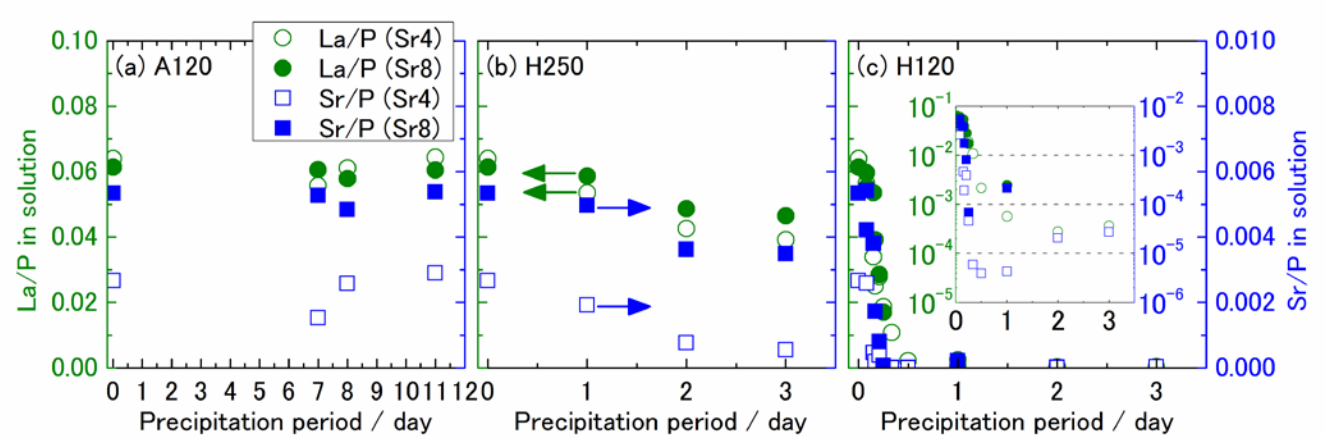

Fig. 5 Change in composition of solutions with time under the conditions (a) A120, (b) H250, and (c) H120. Inset in (c) is a logarithmic plot.

concentrations of La and Sr fluctuated. This is likely due to the fluctuation of water vapor pressure in the atmosphere.

For better understanding of the precipitation behavior, these concentration values were converted into "precipitation ratios." We defined the precipitation ratio of element M, X_M, by the following formula:

$$X_M \equiv \frac{n_{M,\,prec}}{n_{M,\,init}} \times 100\ (\%), \qquad (2)$$

where $n_{M,\,prec}$ and $n_{M,\,init}$ are the quantities of M in the precipitate and initial solution, respectively. For example, X_{La} will be 100 % when all La in the initial solution precipitates as $LaPO_4$. Fig. 6 shows the changes in X_{La} and X_{Sr}. X_{Sr} was greater than X_{La} in the early stages of the precipitation regardless of the initial composition of the solution. This suggests the formation of Sr-richer $LaPO_4$ than the initial solutions.

The Sr doping levels in the $LaPO_4$ precipitates analyzed by ICP, Fig. 7, showed a strong dependence on X_{La}. In good agreement with the precipitation ratio changes described above (Fig. 6), the Sr doping levels in the precipitates were higher in the low X_{La} region, reaching 20 mol% at maximum. This value is one order of magnitude higher than the reported solubilities of Sr in $LaPO_4$. [7,8] The precipitation temperature and pH_2O did not seem to have a significant effect on this trend, although they affect the attainable precipitation ratio limited by thermodynamics, and the Sr doping level accordingly. Thus, it can be concluded that the precipitation method in homogeneous phosphoric acid solutions serves as the most effective synthesis route to date for highly Sr-doped $LaPO_4$.

3.3. Effectiveness of Sr doping

To examine whether Sr was doped correctly and H_2O was incorporated in the bulk as desired, the following two methods were used: (1) The amount of H_2O evaporated from samples at 800 °C in dry N_2 was measured by the Karl Fischer titration method. (2) The unit cell volume of samples was evaluated before and after the H_2O evaporation measurement using

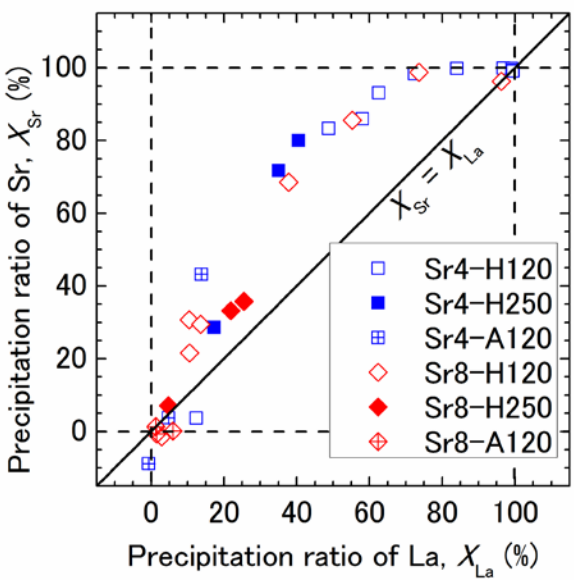

Fig. 6 Change in the precipitation ratios of La and Sr observed along with the progression of the precipitation of $LaPO_4$.

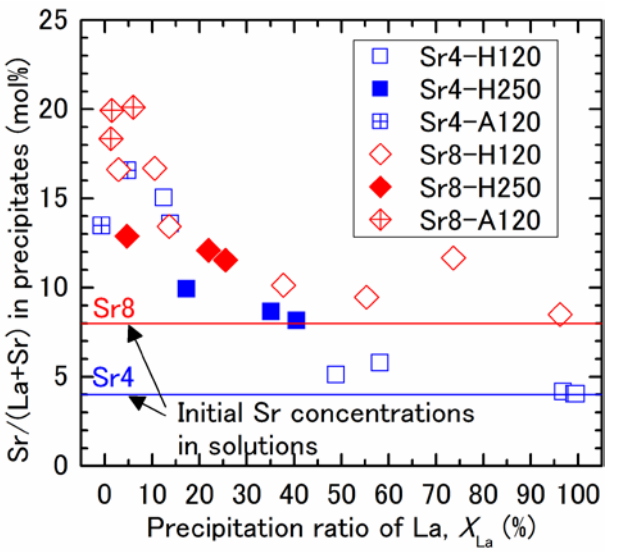

Fig. 7 Dependence of the Sr doping level in $LaPO_4$ on the precipitation ratio of La.

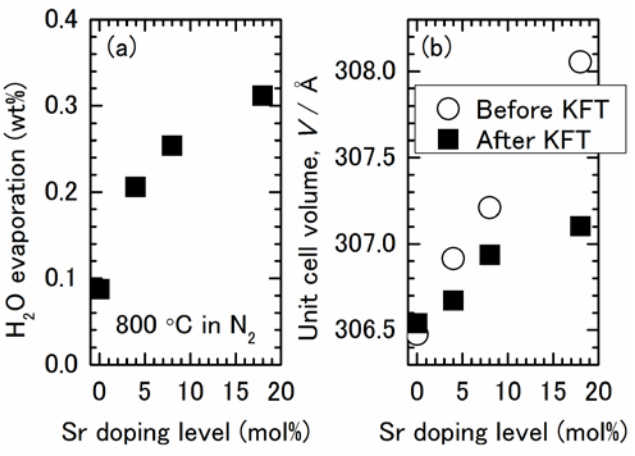

Fig. 8 (a) H_2O evaporation from Sr-doped $LaPO_4$ under N_2 at 800 °C as measured by the Karl Fischer titration (KFT) method. The samples were held in the air at 600 °C for 50 h beforehand. (b) Unit cell volume of Sr-doped $LaPO_4$ as determined by Rietveld analysis using powder X-ray diffraction patterns. The open circles (○) represent the cell volume of samples before the titration (just after held in the air at 600 °C for 50 h). The filled squares (■) represent the cell volume of samples after the titration.

powder X-ray diffraction patterns. Prior to these measurements, samples were dried at 600 °C in the air for 50 h.

Fig. 8 (a) represents the H_2O evaporation from $LaPO_4$ (expressed in percentage of the initial weight of each sample) with different Sr doping levels (0, 4, 8 and 18 mol%). Although the plots are not linear, H_2O evaporation monotonically increased with increasing the Sr doping level. This should indicate that H_2O was incorporated in $LaPO_4$ with Sr on the synthesis. Fig. 8 (b) shows the unit cell volume of samples before and after the H_2O evaporation measurement. In both cases, $LaPO_4$ with higher Sr doping level had larger unit cell volume. This would indicate that Sr substituted for La in the monazite structure, since the ionic radius of Sr^{2+} in ninefold coordination (1.31 Å) is larger than that of La^{3+} (1.21 Å). [14] After the H_2O evaporation measurement, the unit cell volume of Sr-doped $LaPO_4$ significantly decreased while that of undoped $LaPO_4$ remain unchanged. This would reflect the evaporation of H_2O from the bulk Sr-doped $LaPO_4$. In Fig. 8 (a) the small H_2O evaporation was observed even from undoped $LaPO_4$, but it could be due to some residual water on the surface or grain boundaries of the sample.

These results suggest that Sr successfully substituted for La and H_2O was certainly incorporated in the bulk as desired.

3.4. High temperature stability of Sr-doped $LaPO_4$

To evaluate the stability of highly Sr-doped $LaPO_4$, 13.4 % Sr-doped $LaPO_4$ and 20.1 % Sr-doped $LaPO_4$ synthesized in phosphoric acid solutions were heat treated at higher temperatures. The samples were first held at 600 °C for 80 h in the atmosphere, then the 13.4% doped sample was additionally held at 1200 °C for 5 h. Fig. 9 shows the X-ray diffraction patterns obtained after each heat treatment. While no secondary phase was detected after the first heat treatment at 600 °C, the presence of secondary phases, $Sr_2P_2O_7$ and $Sr_3La(PO_4)_3$, was clearly detected after the second heat treatment at 1200 °C. Amezawa *et al*. reported $Sr_2P_2O_7$ as the secondary phase at 1200 °C and $Sr_3La(PO_4)_3$ at above 1350 °C. [6] Tyholdt *et al*. also reported both as the secondary phases at 1450 °C. [8] The detection of both $Sr_2P_2O_7$ and $Sr_3La(PO_4)_3$ in the present study is somewhat incompatible with the previous study by Amezawa but it could be due to some kinetic reason. The present results indicate that the solubility of Sr in $LaPO_4$ would be sufficiently high (at least 20.1 %) at 600 °C, which is in the operating temperature range for the electrolyte. However, the solubility of Sr is considerably lower than

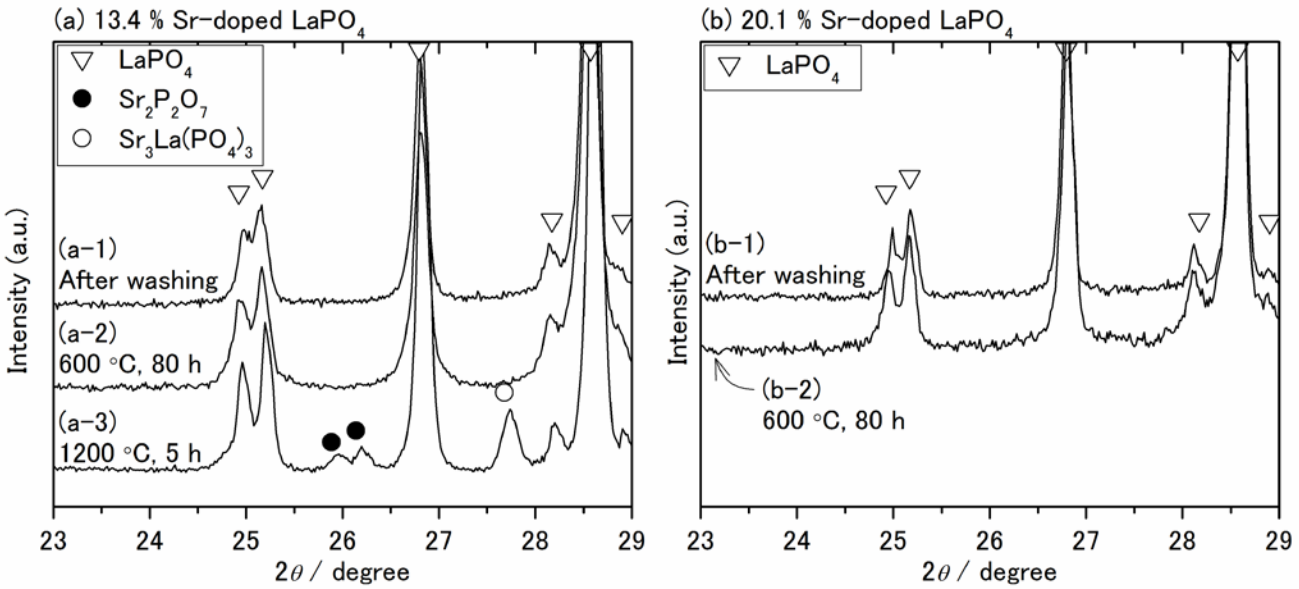

Fig. 9 X-ray diffraction patterns of (a) 13.4% Sr-doped $LaPO_4$ and (b) 20.1% Sr-doped $LaPO_4$. They were collected (a-1)(b-1) just after washing, (a-2)(b-2) after the first heat treatment at 600 °C for 80 h and (a-3) after the second heat treatment at 1200 °C for 5 h. Peaks marked with ▽, ●, and ○ are attributed to $LaPO_4$ (PDF# 1-83-651), $Sr_2P_2O_7$ (PDF#0-24-1011), and $Sr_3La(PO_4)_3$ (PDF# 0-29-1306), respectively.

13.4 % at 1200 °C, which is a typical sintering temperature for this material. Therefore, a new synthesis process of $LaPO_4$ electrolytes based on precipitation in homogeneous phosphoric acid solutions, which enables synthesizing dense $LaPO_4$ electrolytes without sintering, should have a great advantage. The stability of Sr-doped $LaPO_4$ for longer periods will be the subject of future studies.

4. Conclusions

In this study, we investigated the precipitation condition of $LaPO_4$ in phosphoric acid solutions and the morphology of the precipitates. We also studied the optimum condition for obtaining highly Sr-doped $LaPO_4$. Then we examined the effectiveness of doping. Finally we evaluated the stability of Sr-doped $LaPO_4$ at high temperatures. The findings can be summarized as follows:

(1) Increasing pH_2O from 0.01 atm to 1 atm extends the precipitation region of $LaPO_4$ in phosphoric acid solutions toward higher temperatures by nearly 100 °C. It is possible to obtain aggregated $LaPO_4$ crystals up to 200 μm under such conditions (*e.g.* T = 250 °C and pH_2O = 1 atm). This may facilitate the direct synthesis of dense $LaPO_4$ electrolytes in phosphoric acid solutions.

(2) The Sr doping level in $LaPO_4$ shows a strong dependence on the precipitation ratio of La, X_{La}. The Sr doping level is higher in the low X_{La} region, reaching 20 % at maximum. This value is one order of magnitude higher than the previously reported solubilities of Sr in $LaPO_4$.

(3) Sr partially substitutes for La in monazite-type $LaPO_4$ when synthesized in phosphoric acid solutions, as well as by solid state reaction as reported in literature. On synthesis, H_2O is certainly incorporated in the bulk by Sr doping.

(4) The solubility of Sr in $LaPO_4$ would be sufficiently high (at least 20.1 %) even at 600 °C, which is in the operating temperature range for the electrolyte. However, it becomes considerably lower than 13.4 % at 1200 °C.

Acknowledgments

This work was financially supported by MEXT Elements Science and Technology Project and a Grant-in-Aid for JSPS Fellows. The authors would like to thank Mr. Takahito Nakajima at Kyoto University for his experimental assistance.

Notes and references

[a] *Department of Materials Science and Engineering, Kyoto University,Yoshida Honmachi, Sakyo-ku, Kyoto, 606-8501, Japan. Fax: +81-75-753-5284, Tel: +81-75-753-5445, E-mail: materials_process@aqua.mtl.kyoto-u.ac.jp*

1 T. Norby and N. Christiansen, *Solid State Ionics*, 1995, **77**, 240–243.
2 K. Amezawa, S. Kjelstrup, T. Norby, and Y. Ito, *J. Electrochem. Soc.*, 1998, **145(10)**, 3313–3319.
3 S. Gallini, M. Hänsel, T. Norby, M. T. Colomer, and J. R. Jurado, *Solid State Ionics*, 2003, **162–163**, 167–173.
4 G. Harley, R. Yu, and L. C. D. Jonghe, *Solid State Ionics*, 2007, **178**, 769–773.
5 K. Amezawa, Y. Tomii, and N. Yamamoto, *Solid State Ionics*, 2005, **176**, 135–141.
6 K. Amezawa, H. Maekawa, Y. Tomii, and N. Yamamoto, *Solid State Ionics*, 2001, **145**, 233–240.
7 K. Amezawa, Y. Tomii, and N. Yamamoto, *Solid State Ionics*, 2005, **176**, 143–148.
8 F. Tyholdt, J. A. Horst, S. Jørgensen, T. Østvold, and T. Norby, *Surf. Interface Anal.*, 2000, **30**, 95–97.
9 M. T. Schatzmann, M. L. Mecartney, and P. E. D. Morgan, *J. Mater. Chem.*, 2009, **19**, 5720–5722.
10 H. G. Danielmeyer, J. P. Jeser, E. Schönherr, and W. Stetter, *J. Cryst. Growth*, 1974, **22**, 298–302.
11 K. Byrappa, *Prog. Cryst. Growth Charact.*, 1986, **13**, 163–196.
12 N. N. Chudinova, L. P. Shklover, and G. M. Balagina, *Inorg. Mater.*, 1975, **11**, 590–593.
13 G. M. Balagina, N. N. Chudinova, and E. V. Murashova, *Russ. J. Inorg. Chem.*, 2004, **49**, 614–616.
14 R. D. Shannon, *Acta Crysta.*, 1976, **A32**, 751–767.

